Interim Report
for the period
October 1984 to
February 1986

Descriptive Characterization of Solid Ingredients

March 1986

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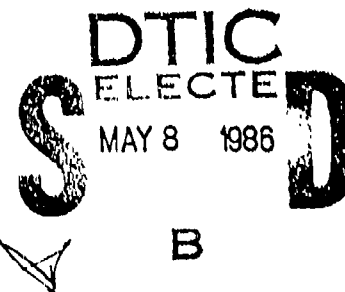
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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Presently weight median diameter measurements are used to correlate oxidizer particle size to ballistic performance in solid propellants. Propellant burning is a heterogenous process that is greatly influenced by available surface area of oxidizer particles. Weight median diameter measurements do not accurately reflect the available oxidizer surface area so there are inherent errors in burn rate correlations. This study focuses on the development of a new oxidizer particle characterization technique that is surface dependent to improve accuracy in correlating oxidizer particles to ballistic performance.

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INTRODUCTION

Before the propellant community can increase its understanding of ingredient behavior in solid propellant combustion, it must increase its knowledge of the ingredients themselves. Propellant combustion is a heterogeneous process and, as such, is greatly influenced by the oxidizer particles' available surface area. The surface area dependence of heterogeneous reactions is used in this study to develop a characterization technique to increase our understanding of oxidizer particle morphological properties and their relation to burn rate in a propellant environment.

At present particle-size-diameter measurements are correlated with ballistic performance. The basis of this correlation is the assumption that the propellant contains spherical smooth particles that relate diameter to surface area and that particle size distribution is consistent. Studies show that particle shape and surface area vary significantly from that of an ideal smooth sphere. B. J. Alley (Ref. 1) has shown that particle diameter measurements often correlate poorly with propellant performance. The most commonly used particle size parameter, the weight median diameter, does not predict particle surface area or size distribution variations. T. P. Rudy and L. S. Bain (Ref. 2) have found that the routine analytical procedures (Mine Safety Appliances Analyzer) used to size ammonium perchlorate (AP) could not detect the distribution variations that caused combustion irstability. Uncertainties concerning particle diameter measurements have led to performance variations which limit the transferability of propellant formulation technology. Formulators often accept a mean diameter within a 10 to 15 micron distribution in propellant formulation and expect these propellants to yield the same relative performance (Ref. 3). Unfortunately, performance may vary up to several percent (Ref. 4). This degree of variation has been accepted because there wasn't a more descriptive characterization method available. E. D. Bosserman (Ref. 4), in a study which correlates AP particle size with burn rate, concluded that the measured parameters closely related to surface area correlated best with burn rate.

To obtain the most valuable information, a method should be developed to produce information that is a function of surface area. Since the burning

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propellant environment consumes the particles, and since the size distribution is interrelated to this consumption (burn rate), this type of consumption-distribution information would be desirable. This consumption-distribution information is related to factors that control burn rate. If particles lose mass at the same mass/surface area rate, smaller particles would naturally be consumed first due to their higher surface area/mass. This produces higher burn rates for smaller particles using propellants with the same solids loading unless other factors act to alter this relationship. Total surface area measurements and size distribution measurements cannot determine if only a portion of the particle distribution's contribution to burn rate is lost due to other factors in the burning process. Combined surface area-distribution information is necessary to determine this partial loss. The most practical method to produce this information would be another heterogeneous consumption system.

The objective of this work is the development of a solid-liquid system that will correlate with the solid-gas system of burning propellant. Before such a method can be developed, a relationship based on surface area dependence must first be established between the heterogeneous solid-gas consumption of a burning propellant system and the solid-liquid consumption of particles dispersed in a liquid system. To liberate a detectable specie for measurement the developed analysis system must not be completely heterogeneous but must interact with the solvent system. This system is initially heterogeneous with surface-area-dependent interaction which allows the particles to be independently consumed into the solution. The system also allows individual particle independence in the same way the burning propellant does (Ref. 5). The particulate oxidizers selected for this study were cyclotetramethylenetetranitramine (HMX), cyclotrimethelenetrinitramine (RDX), ammonium perchlorate (AP), and ammonium nitrate (AN).

Heterogeneous System Comparisons

Numerous studies have attempted to explain combustion behavior (Refs. 6 and 7). Although these studies disagree on reaction dynamics, their models can predict performance reasonably well within a limited range of reaction

conditions. Although any attempt to design such a model is beyond the scope of this work, it is necessary to define a few of the systems' basics to establish a relationship between a solid-gas and solid-liquid heterogeneous system. First, any reaction depends on the availability of reacting species and process initiating energy. In the combustion process this is complicated by the fact that the reacting species is a decomposition product (from HMX, RDX) or dissociated-subliminated species (from AP, AN) which comes from the available oxidizer particle surface area (Refs. 6 and 8). Burn rate increases with temperature, which is ingredient dependent, as well as with pressure (Ref. 8). The rate limiting step, as well as changing with ingredients, may actually vary with the distance the reacting species or energy has to travel to the reaction site. The higher the propellant's uniformity, the shorter these distances become which results in a more uniform burn. It is possible that a lack of uniform oxidizer particle availability may be a limiting factor in correlating oxidizer particle size to burn rate. Since this is a heterogeneous reaction, the higher the surface-area-dependent specie availability, the higher the burn rate unless some other limiting factor changes this relationship. Higher pressures increase burn rate by increasing specie encounter frequency, and shorten the distance to the reaction sites; higher pressures may increase binder melting and may subsequently reduce available oxidizer sublimation/decomposition (Ref. 9). If oxidizer particles are hindered from sublimation/decomposition and are burned beyond the fizz zone of the initial reaction, their burning will not contribute to propellant surface recession so the particles' burning is not a function of propellant burn rate. Particle ejection from the surface to lower burn by coating AP was demonstrated in a work by W. M. Howard, et al (Ref. 10). If sublimation/decomposition hindrance due to ejection or some other mechanism is possible, smaller particles have a higher probability of losing their contribution to the burn rate than do the larger particles due to the thickness of the melt. In fact with HMX at low pressures, the smaller the particle the higher the burn rate, but at higher pressures the larger the particle, the higher the burn rate using indentical solids loading (Ref. 8). AP has a higher burning temperature and requires less energy for significant dissociation/sublimation (Refs. 8 and 11), which may keep AP from the inverse pressure-size relationship of HMX.

Whether the rate limiting step is due to energy transfer or specie transfer should not affect the establishment of these heterogeneous relationships. The proven relationship of particle size to burn rate (Refs. 8 and 11) is evidence that the propellant heterogeneous system has available surface area dependence. The development of a surface-area-dependent analysis for each particle size distribution should allow correlation of surface area to burn rate. The correlation constant will be dependent on energy induction rate, which is pressure and ingredient dependent. The location of a point on a slope of a curve of dissolved specie vs time, as correlated to burn rate, may indicate if hindered sublimation/decomposition of smaller higher-surface-area particles at higher pressures is due to melt interference or to binder-HMX reaction. A correlation at the initial slope may indicate that binder cooling effects or other phenomena produce this relationship. Since the initial slope should be related to the highest-surface-area-per-weight smaller particles, correlation at any other point would indicate that their consumption is not a function of burn rate.

Similar to the solid-gas system of a burning propellant, a solid-liquid system depends on system uniformity for accurate analysis and system correlation. Particle dispersity in the solvent system is dependent on particle size and stir rate. The stir rate must be high enough so that diffusion rate laws are not in effect and must allow complete dispersion of all particles, but low enough that slope changes are easily discerned.

Analytical Method Applicability

Ammonium nitrate and ammonium perchlorate should show relatively complete dissociation of their solvated species in polar solvents (Refs. 12 and 13). This specie independence should allow electrochemical detection of liberated species during interactive-heterogeneous dissolution without disturbing the solvation rate.

HMX and RDX do not readily dissociate in any solvent that would allow electrochemical detection and surface area dependence. However, they do dissolve in solvents that may allow ultraviolet detection of solvated molecules during interactive-heterogeneous dissolution.

Summary of Conclusions from Literature

(1) Propellant burning is a heterogeneous process and is greatly influenced by the available surface area of oxidizer particles.

(2) Weight median diameter measurements do not provide sufficient information for burn rate correlation.

(3) Propellant burning is dependent on the availability of oxidizing species and process initiating energy; the availability of oxidizing species is surface area dependent and requires energy for release.

(4) Combined surface area-distribution information is needed to determine if a partial loss of the contribution of the particulate distribution to burn rate occurs with pressure changes. This is evident since with:

    (a) HMX Propellants - at low pressures the smaller the particle, the higher the burn rate, but at high pressures the larger the particle, the higher the burn rate.

    (b) AP Propellants - the smaller the particle, the higher the burn rate, regardless of pressure.

(5) A solid-liquid heterogeneous consumption system can provide both surface-area-dependent information, and surface-area-distribution information.

(6) The correlation of particle dissolution to burn rate will be pressure and ingredient dependent since burn rate increases with pressure and temperature, and temperature is ingredient dependent.

The following experiments were designed to produce an analytical procedure to establish the correlation between the solid-gas system of a burning propellant and a solid-liquid system of an interactive-heterogeneous dissolution of oxidizer particles. During this first annual reporting period the study has focused on understanding these heterogeneous relationships and generating surface-area-dependence data for AP and AN.

EXPERIMENT

Solution rates in numerous solvents were studied to establish a slowly dissolving system for oxidizer particles. 0.025 grams of oxidizer (HMX, RDX, AP, and AN) were placed in various solvents. Their dispersity and dissolution rates were noted, and time required to complete dissolution was recorded. Then various combinations of these solvents were used to maximize dispersity and slow the dissolution rate to the point where slope changes could be discerned for the smallest possible change in particle size distribution.

AN and AP

The Apparatus. Altex pH meter, model 60; Altex solid state nitrate electrode with double junction reference electrode, Mettler DL40 autotitrator for stirring, Bascom-Turner model 8120T electronic storage recorder, Hiac-Royce particle size analyzer, and ATM sonic sifter.

Reagents. For AP - 50 ml of solvent consisting of 35 ml n-propanol and 15 ml methanol. For AN - 50 ml of solvent consisting of 49 ml of n-butanol and 1 ml of n-propanol. All chemicals were reagent grade.

Operating Procedure. 0.025 grams of oxidizer was placed in 50 ml of the appropriate solvent. A plot of millivolts vs time was recorded for each available particle size distribution. Particle size distributions and specific surface area calculations of these particle size distributions were performed as a comparison tool. Table 1 shows the weight median diameters marked on the containers as received and used by formulators, and weight median diameters as reanalyzed by the Hiac particle size analyzer and ATM sonic sifter, and calculated mean specific surface areas derived from that data.

TABLE 1. PARTICLE SIZE DISTRIBUTIONS USED
(mean diameter in microns)
(mean specific surface area in m²/gm)

			AP				
As received	0.5	1.8	16	50	100	200	400
Hiac/Sieve	13	11	29	25	53	200	400
Specific surface area	0.27	0.31	0.14	0.13	0.077	0.017	0.008
			AN				
As received	13	14	16	17	50	67	160
Hiac/Sieve	13	15	32	24	43	211	155
Specific surface area	0.29	0.25	0.14	0.19	0.099	0.018	0.021

RESULTS AND DISCUSSION

AP and AN. As seen in Figures 1 and 2 both AP and AN do show surface area dependent dissolution in the chosen solvent systems. These figures use the weight median diameters as received. As drawn using semi-log paper Figures 1 and 2 show that as the mean diameter increases, there is strong evidence of the higher surface area contribution of the smaller particles in the normal particle distributions. This phenomena is especially evident with AN. Using AP particles with a narrow distribution the curve appears to be more linear. When monodispersed AN particles are used later in this program, it should be proven whether this is the result of the distribution or other phenomena. Data for 0.5 micron AP was discarded once it was learned the AP had a paraffin coating. In Figures 3 and 4 the same particle size distributions are used in a calculated mean specific surface area parameter vs solution rate plots. These plots provide evidence of surface area dependence for these interactive heterogeneous systems. This greater linearity indicates that the surface area dependence, which the distributions display, reveals the degree of disparity between the mean diameter and surface area measurements for normal distributions. The absence of perfect linearity and the apparent data point variations, may be due to particle shapes that change with changes in size, grinding method, and crystalline phase stabilization additives. Initial surface area analysis performed on demonstration equipment indicates that actual surface area is much larger than the calculated values based on
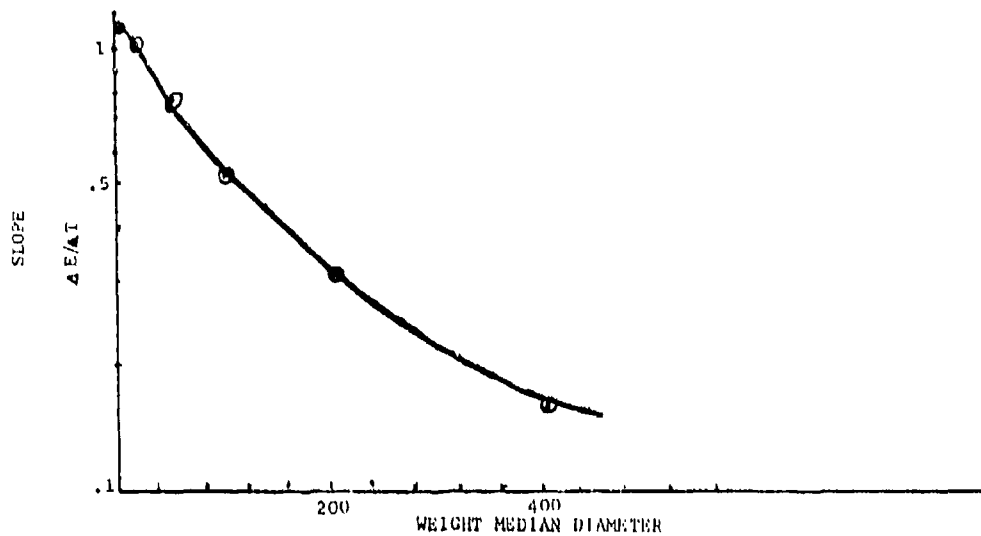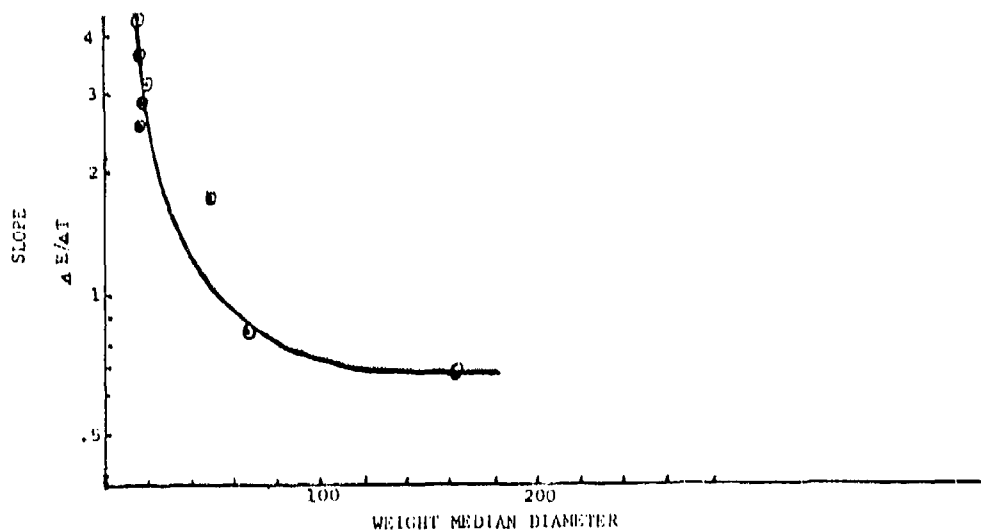
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Figure 1. AP, Size vs Solution Rate.

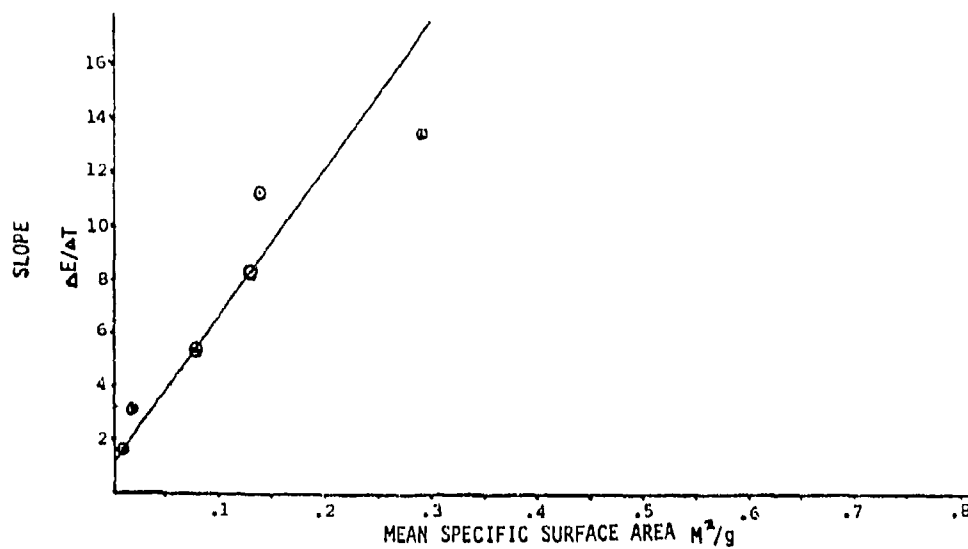Figure 2. AN, Size vs Solution Rate.

Figure 3. AP, _Mean Specific Surface Area vs Solution Rate._
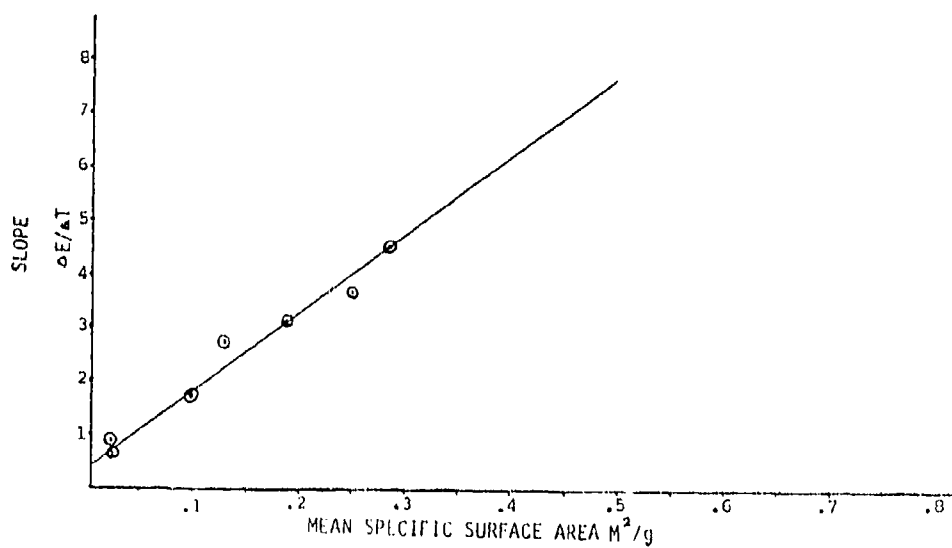

Figure 4. AN, _Mean Specific Surface Area vs Solution Rate._

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spherical particles. Since sh-pe variation should actually affect burn rate, this data may lead to significant burn rate correlation improvement. The correlation coefficient for AN is 0.989 and for AP is 0.931. Discarding data for 1.8 micron AP because Hiac data for such small sizes has been known to be unreliable would improve the correlation constant for AP to 0.959.

Figure 5 shows an actual plot of AP using half 16 micron AP and half 100 micron AP. There is an easily discerned slope break seen as the smaller AP is consumed. I would not expect to see this type of slope break with particles much closer in size, but computer manipulation of the data may indicate where large populations of particles are consumed. This method may be used to correlate the time for dissolution to a particle consumption point to mean particle diameter measurements. Individual 0.025-gram samples of 16 micron AP and 100 micron AP are shown in time vs millivolt plots, but the plot scales are not identical with the bimodal plot. AN's slope break is not shown because it is not as easily discerned for the size distributions analyzed. Microscopic examination showed agglomeration for both AP and AN samples, but in unstabilized AN particles, the agglomeration was severe making distributions extremely broad. Perhaps use of monodispersed particles would display this slope break for AN. In both cases the slope should constantly decrease with particle dissolution; larger decreases should occur where large populations are consumed. Unfortunately electrode noise and electrode stability/starting millivolt variation problems may obscure some of this data.

CONCLUSIONS AND RECOMMENDATIONS

Surface area dependent data can be generated from an interactive heterogeneous system and correlated to burn rate. AP and AN can produce such data in the solvent systems chosen.

FUTURE WORK

Monodispersed particles will be isolated for use in correlations and calibrations. Conductivity measurements will be attempted to see if nitrate electrode stability problems can be solved for AN and AP. HMX and RDX systems
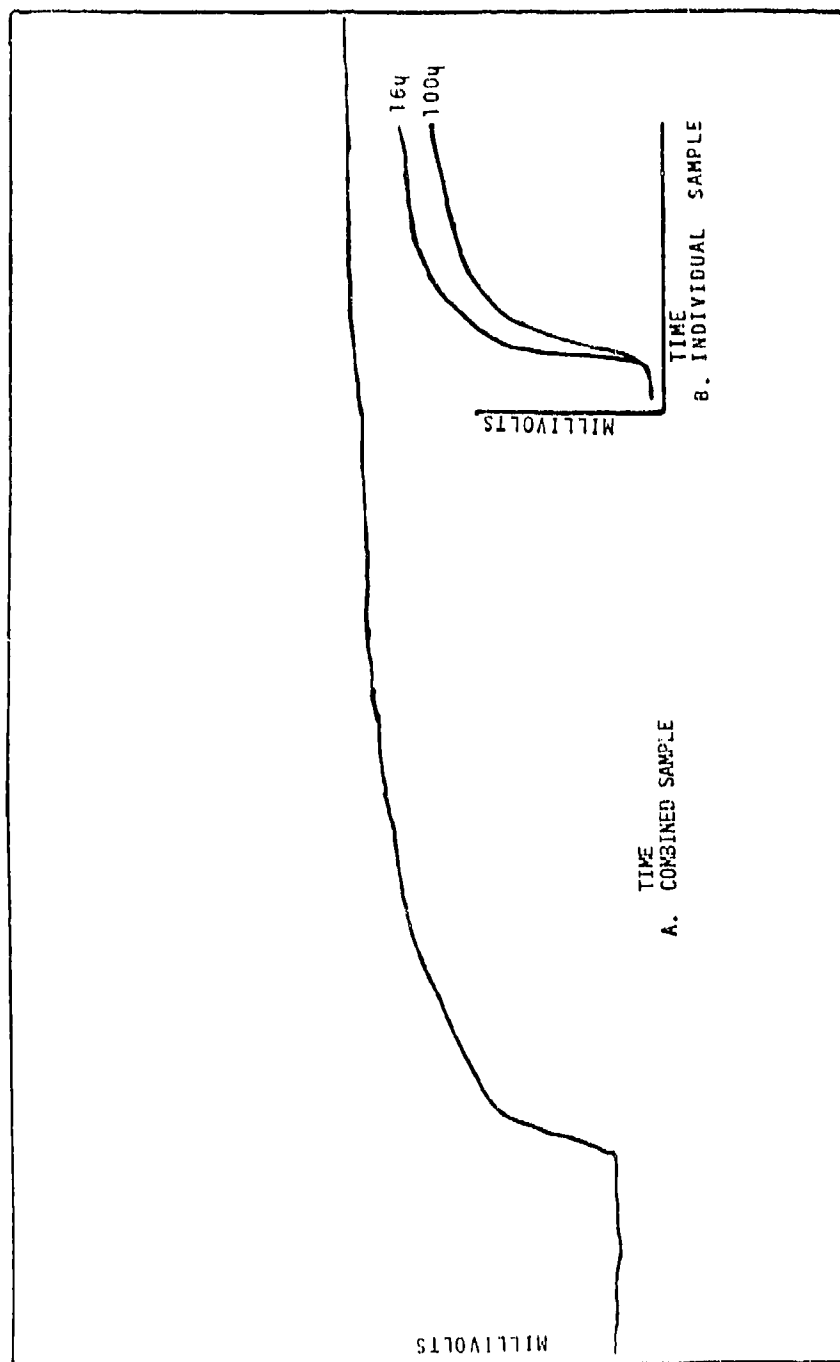
Figure 5. AP, 16 and 100 Micron Data Plots.

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will be developed using interactive heterogeneous dissolution and UV detection. If that fails, other systems will be explored. Surface area analyses will be attempted on all particle distributions analyzed. Finally burn rate correlations will be made for a series of propellants and strand burn rates.

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